EQUILIBRIUM MODELLING OF A BIOSORPTION SYSTEM CONSISTING OF A BACTERIAL BIOFILM SUPPORTED ON GAC FOR REMOVAL OF CHROMIUM (VI) AND ORGANIC COMPOUNDS FROM AQUEOUS SOLUTION

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The removal of heavy metals and organic compounds like phenol, chlorophenol and o-cresol from wastewater, is one of the most important environmental problems yet to be solved. The retention of these contaminants by a biofilm supported on granular activated carbon is a promising technology for the treatment of diluted solutions, as the biofilm is able to retain the metallic ions and the support will help to fix them for further catalytic applications. In continuous processes, the time for breakthrough and the shape of the breakthrough curve are very important characteristics for the description of the operation and of the dynamic response of a biosorption column. Mechanistic models may be developed combining the active site mass balances with the equilibrium constants of complex formation of the assumed site-ion reactions (Pagnanalli, 2003a, 2003b, 2004; Veglió, 2003). A modelling approach for an expanded bed biosorption system is presented using the ADR (Advection-Dispersion-Reaction) equation as the basis of the mathematical description. The parameters used for characterizing the expanded bed biosorption and for implementing the model are: geometrical dimensions of the bed, packing arrangement, operating conditions of the system and sorptive characteristics of the biosorbent material. Several biosorption studies were made using a bacterial biofilm of *Arthrobacter viscosus* supported on granular activated

carbon in a mini-column arrangement and the obtained data were compared with the predicted by the model. The initial chromium (VI) and organic compound concentration was 100 mg/l.

Theorectical

The applicability of the well known Advection-Dispersion- Reaction (ADR) equation as the basis for the simulation of experimental biosorption breakthrough curves in the form of a simple and yet reliable tool is one of the aims of this work. The equation has been applied under the concept of rapid local equilibrium and for this reason only the ADR equation and the appropriate biosorption isotherm are necessary to describe the whole system. The referred equation (Weber Jr. *et al.*, 1991), simplified in one dimensional form for a single solute, subject only to sorption without any other fluid-phase reaction or source term, is presented:

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial Z^2} - u_z \frac{\partial C}{\partial Z} - \frac{\rho_s (1-\varepsilon)}{\varepsilon}\left(\frac{\partial q}{\partial t}\right) \qquad (1)$$

This equation incorporates the diffusive and bulk solute movement in the first two terms and the sorptive process in the third term. The solution of the ADR equation in space and time describes the performance and process dynamics of a sorption packed column, by predicting the corresponding breakthrough curve, that is the effluent solute concentration-time profile.

The term $\partial q/\partial t$ represents the rate of the solute uptake by the biosorbent material and is the most important term of the solute material balance. The most simplistic approach to model sorption phenomena is to assume that the time scale associated with the microscopic processes of mass transfer to the sorption sites and the subsequent sorption reaction time are much smaller than that associated with the macroscopic processes of fluid transport. This effectively assumes that equilibrium prevails locally and is approached rapidly. Under this concept, the rate of change of the sorbed phase concentration, q, at any point z, is

instantaneously reflected by the rate of change of the solution phase concentration, C, at any point. Therefore, it is assumed that mass transfer resistances in the liquid and solid phases are negligible and the biosorption reaction is instantaneous. This approach yields the so-called local equilibrium models (LEM) and incorporates only the isotherm in Eq. (1), overlooking the rate at which the equilibrium is approached (Hatzikioseyian *et al.*, 1991).

The LEM model assumes that the equilibrium distribution between the solid phase and the fluid phase is linear. Because of that, a linear isotherm equation is applied (Eq. (2)), and the partial derivative $\partial q/\partial t$ can be substituted by the partitioning coefficient K_P (Eq. (3)). The partial derivative $\partial q/\partial t$ is equal to the total derivative dq/dC times $\partial C/\partial t$ as q is only a function of C in all isotherm models used subsequently.

$$q = K_p C \tag{2}$$

$$\frac{dq}{dC} = Kp \tag{3}$$

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial Z^2} - u_z \frac{\partial C}{\partial Z} - \frac{\rho_S (1-\varepsilon)}{\varepsilon} Kp \left(\frac{\partial C}{\partial t} \right) \tag{4}$$

The linear local equilibrium model (LLEM) represented in Eq. (4), is very popular for column configurations, due in part to the relative simplicity of its solution, which can be obtained analytically and differs simply by a constant from any solution to the conservative form of the ADR equation. Although the LLEM version of ADR equation has been widely employed to describe solute retardation by sorption, it became apparent that this model frequently fails to provide adequate representation of the effect of sorption processes on solute transport. Inclusion of the more sophisticated nonlinear equilibrium models, such as the Freundlich or

Langmuir, often provides better representation of sorption phenomena, especially over extended equilibrium concentration ranges (Weber Jr. *et al.*, 1991).

When the Langmuir isotherm (Eq. (5)) is used to describe sorption, the local equilibrium model is obtained by substituting the term $\partial q/\partial t$ by Eq. (6) times $\partial C/\partial t$.

$$q = \frac{Q^0 bC}{1+bC} \tag{5}$$

$$\frac{dq}{dC} = \frac{Q^0 b}{(1+bC)^2} \tag{6}$$

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial Z^2} - u_z \frac{\partial C}{\partial Z} - \frac{\rho_S (1-\varepsilon)}{\varepsilon}\left(\frac{Q^0 b}{(1+bC)^2}\right)\left(\frac{\partial C}{\partial t}\right) \tag{7}$$

where Q^0 (mg/g) is the maximum amount of metal ion per unit weight of biosorbent to form a complete monolayer on the surface bound at high C, and b (l/mg) is a constant related to the affinity of the binding sites. Q^0 represents a practical limiting adsorption capacity when the surface is fully covered with metal ions (Akzu, 2001). Q^0 and b can be determined from the linear plot of C/q versus C.

For the case of the Freundlich model (Eq. (8)), the term $\partial q/\partial t$ can be substituted by the derivative of the Freundlich model (Eq. (9)) times $\partial C/\partial t$.

$$q = K_F C^n \tag{8}$$

$$\frac{dq}{dC} = K_F n C^{n-1} \tag{9}$$

$$\frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial Z^2} - u_z \frac{\partial C}{\partial Z} - \frac{\rho_S (1-\varepsilon)}{\varepsilon} K_F n C^{n-1} \left(\frac{\partial C}{\partial t} \right) \qquad (10)$$

where K_F is an indicator of adsorption capacity and n indicates the adsorption intensity. The Freundlich constants can be determined by the logarithmic form of equation (8).

Equations (7) and (10) were solved using the software package PDECOL in Fortran (Madsen and Sincovec, 1979) and the parameters are presented on Tables 1.

Table 1- The Langmuir constants and Freundlich constants obtained from Langmuir adsorption isotherms and Freundlich adsorption isotherms for chromium and for organic compounds

	Q^0 (mg/g)	b (l/mg)	R^2
Chromium	5.82	0.57	0.99
Chlorophenol	256.41	0.09	0.83
Phenol	23.15	0.20	0.98
O-Cresol	90.09	0.51	0.97
	K_F ($l^n mg^{n-1} g^{-1}$)	n	R^2
Chromium	1.36	3.43	0.97
Chlorophenol	2.66	4.44	0.85
Phenol	2.77	0.68	0.84
O-Cresol	4.40	6.48	0.90

Results and discussion

There are clear differences in the adsorption behaviour of phenol, o-cresol and chlorophenol (Figure 1 and 2). The differences in molecular size, solubility, dissociation equilibrium and benzene ring reactivity, can explained this (Streat *et al*., 1995, Brasquet *et al*., 1997). This system showed best results for the chlorophenol and o-cresol than for phenol and chromium.

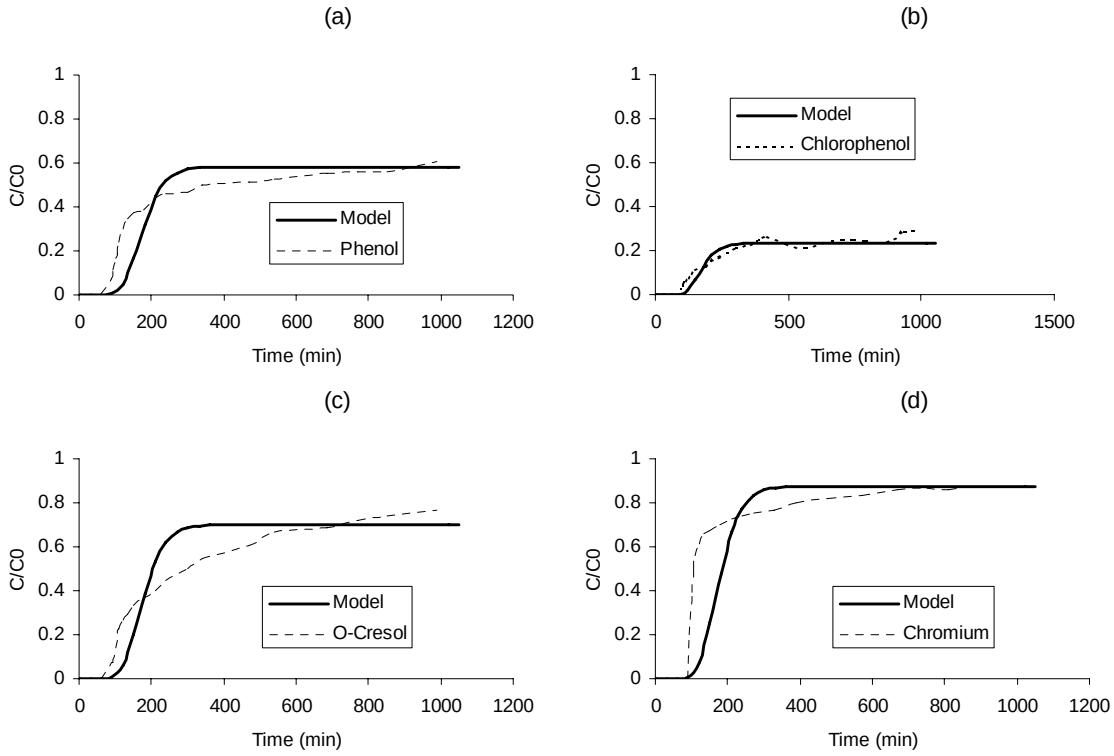

Figura 1- Comparison between the experimental results and those predicted by the model using the parameters calculated from the Langmuir isotherm model. The inlet solute concentration was 100 mg/l. (a) Phenol, (b) Chlorophenol, (c) O-Cresol and (d) Chromium.

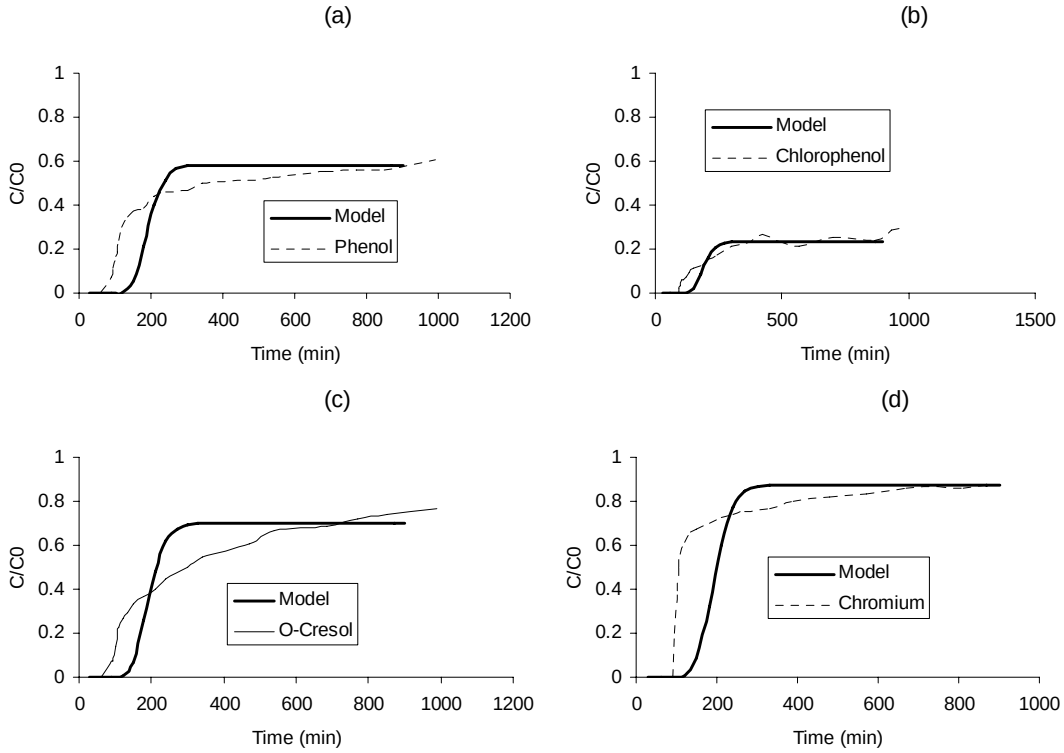

Figura 2- Comparison between the experimental results and those predicted by the model using the parameters calculated from the Freundlich isotherm model. The inlet solute concentration was 100 mg/l. (a) Phenol, (b) Chlorophenol, (c) O-Cresol and (d) Chromium.

It was observed that for chlorophenol results were fitted reasonably well by both models. For the other compounds tested, phenol, o-cresol and chromium, the model presents best results when the parameters of the Langmuir isotherm were used. The shift between the experimental results and those predicted by both models seems to be related with the metabolic activity which is not quantified and consequently is not introduced on the model.

Nomenclature

A- section area, m^2

b- Langmuir adsorption constant, mg/g

C- concentration in fluid, mg/l

C_0- inlet solute concentration, mg/l

$C_{i,calc}$- calculated concentration for a point i, mg/l

$C_{i,exp}$- experimental concentration for a point i, mg/l

Dh- apparent column dispersion coefficient, m^2/s

F- volumetric flow rate, m^3/s

K_F- Freundlich adsorption constant, mg/g

K_P- partitioning coefficient, l/g

L- lenght of column, m

n- Freundlich adsorption constant

N- number of measurements

q- adsorbed quantity, mg/g

Q^0- Langmuir adsorption constant, mg/g

U_Z- interstitial fluid velocity ($U_Z = F/A*\varepsilon$), m_3/s

Z- axial distance from column inlet, m

ε- bed void volume (space volume/total volume)

ρ_S- density of GAC, Kg/m^3

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